

(12) Laid Open Patent Publication (A)

(19) Japan Patent Office (JP)

(11) Patent Application Publication Number

2002-293903
(P2002-293903A)

(43) Laid Open: Heisei 14 Oct.9 (2002, Oct.9)

(51) Int. Cl. ⁷ C 08 G 63/78	Classification symbol	FI C 08 G 63/78	Theme code (reference) 4J029
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Examination request: Not requested	Number of claims: 4	OL	(Total 6 pages)
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(21) Patent application No.: 2001-92794 (P2001-92794)

(22) Filing date: Heisei 13 Mar. 28 (2001, March 28)

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(54) [Title of invention] Cyclic Polyester Oligomer Production Method and Polyester
Production Method

(57) [Abstract] (with corrections)

[Issues]

A production method of cyclic polyester oligomers in which, in a production of polyester with a high degree of polymerization, an economic efficiency is enhanced compared to that of prior art production methods.

[Means of Resolution]

A production method of cyclic polyester oligomers wherein in producing cyclic polyester oligomers, straight polyester oligomers with which when an esterification reaction of dicarboxylic acid and diol is conducted, a starting mole ratio between diol components and dicarboxylic acid components is in the range of 1.0 ~ 1.6. Further, a method to produce polyester in which obtained cyclic polyester oligomers are open-ring polymerized and thereby polyester is produced.

[What is claimed is:]

[Claim 1]

A method to produce cyclic polyester oligomers in which an esterification reaction of dicarboxylic acid components and diol components is conducted with a starting mole ratio (diol components/ dicarboxylic acid components) of 1.0 ~ 1.6 to obtain straight polyester oligomers and then from said straight polyester oligomers, cyclic polyester oligomers are produced.

[Claim 2]

The production method of cyclic polyester oligomers according to claim 1, wherein an average polymerization degree of straight polyester oligomers is 2 ~ 30.

[Claim 3]

The production method of cyclic polyester oligomers according to claim 1 or claim 2, wherein diol components with which an esterification reaction is conducted are mainly at least one material which is selected from ethylene glycol, propanediol and butanediol.

[Claim 4]

A method to produce polyester in which cyclic polyester oligomers according to any one of claim 1 through claim 3 are brought into contact with a catalyst for cyclic polyester oligomers and an open ring polymerization is conducted.

[Detailed Explanation of the Invention]

[0001]

[Technical Field of Invention]

The present invention pertains to an economical production method of cyclic polyester oligomers using straight polyester oligomers obtained through an esterification reaction of dicarboxylic acid and diol.

[0002]

[Prior Art Technologies]

Because of its excellent properties, polyester is used for a wide variety of areas such as for fibers, films and bottles. In particular, polyalkylene terephthalate is superior in its mechanical strength, chemical properties, dimensional stability and so forth, and thus it is preferably used. Besides, among its uses, for example, for fibers to be used in industrial materials, a high degree of strength is required. Therefore, methods to improve the fiber strength through making the molecular weight of polyalkylene terephthalate higher is suggested.

[0003]

Generally, polyalkylene terephthalate is produced from terephthalic acid or its ester formation derivative and alkylene glycol, but in a commercial process to manufacture polymers with a high molecular weight, a method in which a melt polymerization is conducted and then a solid phase polymerization is conducted to obtain a high degree of polymerization is widely applied. However, a method to obtain a high degree of polymerization through a solid phase polymerization has some undesirable characteristics such as those which are described below.

[0004]

For instance, in order to conduct a solid phase polymerization, there is a large increase in the cost for facilities such as a process for drying polyester chips. Moreover, the residence time of chips is long. Therefore, large improvements in its productivity are desired.

[0005]

For these issues, for instance in publication No. WO96/ 22319, a method is proposed in which polyethylene terephthalate prepolymer in a molten state and having a polymerization degree of 5 ~ 35 is cooled at 120 ~ 210 degrees Celsius, then pelletized and crystallized at the same time, or in which non-quality polyethylene terephthalate prepolymer in a pellet form having a polymerization degree of 5 ~ 35 is rapidly heated to 120 ~ 210 degrees Celsius and then crystallized, and a solid phase polymerization is conducted at 230 ~ 240 degrees Celsius to give polyethylene terephthalate prepolymer. With these methods, a melt polycondensation process is eliminated and a solid phase polymerization is conducted. Thereby it proposes a reduction of facility costs. Facility costs are saved by skipping the melt polycondensation. However, in order to obtain a higher polymerization degree of polyethylene terephthalate, a substantial reaction time is required in a solid phase polymerization process. Therefore, these methods are insufficient in order to improve the productivity of prior art methods.

[0006]

On the other hand, open ring polymerization reactions using cyclic polyester oligomers are attracting attentions. For example, regarding the open ring polymerization of cyclic polyester oligomers described in Macromolecules (Brunelle, 31 (4782), 1998), it is reported that polymer having a high degree of polymerization can be obtained in a very short period of time. In the report, diol and terephthaloyl chloride are employed as source materials and condensation is conducted under a presence of an amine catalyst which does not have steric hindrance, thereby preparing cyclic polyester oligomers. However, prior art methods using an amine catalyst and corrosive acid chlorides such as terephthaloyl chloride are not preferable because those methods require chlorides that are disadvantageous in terms of the environment. In addition, an expensive recirculation process is required in relation to the formation of amine salt which is a byproduct.

[0007]

Furthermore, macrocyclic polyester oligomers proposed in Japanese Laid Open Patent Publication No. H8-225633 exhibit a low degree of intrinsic viscosity, and can be easily impregnated in a fine fibrous preform. Hence, they are receiving attentions as a matrix for composite materials. In addition, macrocyclic polyester oligomers are molten and polymerized at a much lower temperature than polymers to be obtained. Therefore, a molten flow, polymerization and crystallization can take place isothermally. Accordingly, it is pointed out that less time, costs and tools are required for thermal recycling. However, regarding the source material synthesis of straight polyester oligomers that are the source materials of cyclic polyester oligomers, the prior art publication only discloses dimethyl terephthalate and butanediol. Using dimethyl terephthalate, which is an expensive source material, is not sufficient to improve the economical efficiency and the productivity of prior art methods using a solid phase polymerization. In addition, in the case in which dimethyl terephthalate is employed as a source material, the reactivity decreases when the starting mole ratio of diol components/ dicarboxylic acid derivative components is 1.6 or lower, and thus it is not desirable. On the other hand, when the starting mole ratio is set higher than 1.6, the average polymerization degree of obtained straight polyester oligomers drops. In order to reach a preferable average polymerization degree, excessive diol should be removed. Therefore, the productivity decreases after all and thus it is not desirable considering an economic efficiency.

[0008]

Further, the production method of macrocyclic polyester oligomers proposed in Japanese Laid Open Patent Application Publication No. H9-296036 is to bring straight polyester into contact with an organic solvent which does not substantially contain oxygen or water and a depolymerization catalyst,

thereby depolymerizing the straight polyester, and generating macrocyclic polyester oligomers. An amine catalyst and conventionally known corrosive acid chlorides such as terephthaloyl chloride are not used in this method and hence, it is advantageous in the environmental aspect. However, in the method to obtain cyclic polyester oligomers through depolymerizing straight polyester, reaction control is difficult and thus in order to conduct a stable production, costs for incidental facilities are required. Therefore, it is insufficient to improve the economical efficiency.

[0009]

Based on the background described in the above, it is desired to economically obtain polyester with a high degree of polymerization.

[0010]

[Issues that the Invention Attempts to Solve]

The purpose of the present invention is to eliminate the disadvantages in a synthesis of cyclic polyester oligomers mentioned in the above, and to provide an economical production method of cyclic polyester oligomers.

[0011]

[Means to Solve Issues]

The aforementioned purpose of the present invention is accomplished by a production method of cyclic polyester oligomers and polyester in which an esterification reaction of dicarboxylic acid and diol is conducted with a starting mole ratio (diol components/ dicarboxylic acid components) of 1.0 ~ 1.6 to obtain straight polyester oligomers, and from said straight polyester oligomers, cyclic polyester oligomers and polyester are produced.

[0012]

[Embodiments of the Invention]

As concrete examples of dicarboxylic acid components that are used for the esterification reaction of the present invention, aromatic dicarboxylic acids including terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid and 4, 4'-diphenyl dicarboxylic acid, aliphatic dicarboxylic acids such as adipic acid and sebacic acid, and alicyclic dicarboxylic acids including cyclohexane

dicarboxylic acid can be listed. Besides, examples of diol components include ethylene glycol, propanediol, butanediol, neopentyl glycol, hexamethylene glycol, dimethylene glycol, polyethylene glycol, polypropylene glycol and cyclohexane diethanol.

[0013]

Concrete examples of polyester to be obtained in the present invention include polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polycyclohexylene dimethylene terephthalate, polyethylene-2, 6-naphthalene dicarboxylate, polyethylene-1, 2-bis (2-chlorophenoxy) ethane-4, and 4'-dicarboxylate. The present invention is especially suitable with polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate that are widely used, or with polyester copolymers that mainly contain polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate.

[0014]

Polyester to be obtained in the present invention is not particularly limited as long as it can be used as shaped products such as fibers, films and bottles and the like.

[0015]

Furthermore, to such polyester, as copolymerization components, dicarboxylic acids and their ester formation derivatives such as adipic acid, isophthalic acid, sebacic acid, phthalic acid, and 4, 4'-diphenyl dicarboxylic acid, dioxy compounds such as polyethylene glycol, diethylene glycol, hexamethylene glycol, neopentyl glycol and polypropylene glycol, oxycarbonic acids and their ester formation derivatives including p-(-oxyethoxy) benzoic acid and lactic acid may be copolymerized.

[0016]

It is necessary to set the starting mole ratio (diol components/ dicarboxylic acid components) in the esterification of the present invention as 1.0 ~ 1.6. Here, in the case in which the starting mole ratio of diol components/ dicarboxylic acid components is 1.0 or lower, the productivity decreases because a longer time period is required for the esterification reaction, and thus it is not desirable. On the other hand, when the starting mole ratio is 1.6 or higher, the average polymerization degree of straight polyester oligomers obtained through the esterification reaction drops. Hence, cyclic polyester oligomers that provide polyester with a high polymerization degree cannot be obtained. Besides, in order to achieve a preferable average polymerization degree, excessive diol components should be

removed. Therefore, the productivity decreases after all. The starting mole ratio of diol components/dicarboxylic acid components is more preferably 1.1 ~ 1.5, and the starting mole ratio of 1.25 ~ 1.40 is even more desirable.

[0017]

In the cyclic polyester oligomer production method of the present invention, it is preferred that straight polyester oligomers are obtained through a continuous polymerization process. Here, the continuous polymerization process includes three or more tanks including a prior art esterification reaction tank, a preliminary polymerization tank and a final polymerization tank. Straight polyester oligomers are those which passed through the esterification reaction tank in which the esterification reaction is substantially completed, or straight polyester oligomers which passed through the subsequent preliminary polymerization tank may be used. At this point, for a method of polycondensation in the preliminary polymerization tank, any one of the prior art methods can be applied. For instance, a method in which while raising the temperature of a reaction product under a reduced pressure, leaving diol components and other byproducts and the like are removed, and at the same time, a polymerization degree is increased up to a predetermined value can be applied. Or a method in which instead of reducing a pressure in a reaction system, an inert gas is supplied to increase a polymerization degree is increased and so forth can be applied.

[0018]

Further, it is preferred that the average polymerization degree of straight polyester oligomers of the present invention is 2 ~ 30. More desirably, the average polymerization degree is 2 ~ 10 and even more preferably it is 2.5 ~ 4.0. In order to obtain a desirable straight polyester oligomers, it is preferred to use those which passed through an esterification reaction tank in an continuous polymerization process. Regarding such a continuous polymerization process, a method may be employed in which, in a continuous polymerization apparatus in that a prior art melt polycondensation process is conducted, a branch pipe is provided for a reaction product solution transfer pipe between the esterification reaction tank and a preliminary polymerization tank, and the amount of solution transfer is controlled with a gear pump and so forth.

[0019]

In the present invention, at any point before the formation of straight polyester oligomers, esterification catalysts are added to a reaction system, and thereby a reaction speed of an esterification reaction is improved further. As for specific compounds of esterification catalysts, various types of prior art compounds can be employed. Tin compound and/ or titanium compound that are known to have an esterification catalytic activity are particularly desirable. Furthermore, any point before the formation of straight polyester oligomers indicates any point at the time of preparation of slurry of dicarboxylic acid and diol, and in the esterification reaction process.

[0020]

Examples of tin compound include, dibutyl tin oxide, stannous chloride, tin octylate, tin laurilate and monobutyl hydroxy tin oxide and so forth. These tin compounds can include those in which a plurality of tin compound molecules are associated or those which became oligomers with some changes.

[0021]

Moreover, as titanium compound, tetrabutyl titanate, tetraisopropyl titanate, tetrastearyl titanate, potassium titanyl oxalate, lithium titanyl oxalate and the like can be listed. Among them, a complex oxide whose main metallic element is a titanium compound, and a compound containing chelating agents whose main metallic element is a titanium compound are particularly preferred. Here, a complex oxide whose main metallic element is a titanium compound is, for example, produced from a titanium alkoxide compound and alkoxide compounds such as silicon, aluminum, zirconium, and germanium through the sol-gel process of coordination chemistry, however, it is not particularly limited. Furthermore, a compound containing chelating agents whose main metallic element is a titanium compound is, for instance, a titanium compound containing chelating agents such as ethylenediamine tetraacetic acid, hydroxy ethyl iminodiacetic acid, diethylenetriamine pentaacetic acid, triethylene tetramine hexaacetic acid, citric acid, maleic acid or a mixture of these, however, it is not particularly limited.

[0022]

In addition, considering a reaction speed of an esterification reaction and a hue of polymers to be obtained in the end, the amount of esterification catalysts to be added is preferably 0.0001% by weight ~ 0.2% by weight in metal weight against polymers to be obtained. Further, it is even more desirable to be 0.0005% by weight ~ 0.1% by weight.

[0023]

As long as straight polyester oligomers that are specified in the present invention are used, for a production method of cyclic polyester oligomers, prior art methods can be employed and methods are not particularly limited.

[0024]

For instance, regarding a reaction solvent and a cyclization catalyst, for instance in the synthesizing method of cyclic polyester oligomers described in Polymer Letters (F. Lynn Hamb, 5 (1057), 1967), it is reported that as a solvent 1-methylnaphthalene is used, and as a cyclization catalyst tetraisopropyl titanate is used. Furthermore, Japanese Laid Open Patent Application Publication H8-225633 proposes to employ a hydrocarbon compound such as ortho-terphenyl, meta-terphenyl or para-terphenyl and the like as a solvent, and an organic tin compound and or a tetraalkoxy titanate including tetrabutyl titanate as a cyclization catalyst. Therefore, a hydrocarbon compound such as α -methylnaphthalene, ortho-terphenyl, meta-terphenyl or para-terphenyl and the like can be used as a solvent in the present specification, an organic tin compound and or a tetraalkoxy titanate and the like can be employed as a cyclization catalyst, and it is not particularly limited. Besides, in view of a reaction speed of cyclization reaction and an economical efficiency, the amount of cyclization catalysts to be added is preferably 0.01% by weight ~ 2% by weight in metal weight against cyclic polyester oligomers to be obtained. Further, it is more desirable to be 0.1% by weight ~ 1% by weight.

[0025]

Cyclic polyester oligomers to be obtained through the production method of the present invention are substantially pure, and the purity is 60% or more.

[0026]

In producing polyester through an open ring polymerization using cyclic polyester oligomers of the present invention, cyclic polyester oligomers can be brought into contact with catalysts for cyclic polyester oligomers, and not particularly limited.

[0027]

For instance, various types of organic tin compounds and titanate ester described in U.S. Patent Publications Nos. 5039783, 5214158 and 5231161 can be employed as catalysts for cyclic polyester oligomers, or cyclic titanium catalysts including di-(1-butyl)-2, 2-dimethylpropane-1, 3-dioxy titanate, bis (2, 2-dimethyl-1, 3-propylene) titanate or 1-(1-butoxy)-4-methyl-2, 6, 7-trioxa-1-titanabicyclo [2, 2, 2] octane may be used as catalysts for cyclic polyester oligomers. In addition, antimony compounds and bismuth compounds mentioned in Macromolecules (Ji H. Youk, 33 (3594), 2000) can be employed as catalysts for cyclic polyester oligomers, but they are not particularly limited.

[0028]

Furthermore, in view of a reaction speed of an open ring polymerization and a polymerization degree of generated polymers, the amount of catalysts for cyclic polyester oligomers to be added is preferably 0.0001% by weight ~ 1% by weight in metal weight against polymers to be obtained. Further, it is more desirable to be 0.001% by weight ~ 0.3% by weight.

[0029]

When cyclic polyester oligomers of the present invention are brought into contact with catalysts for cyclic polyester oligomers, temperatures in the range of 160 ~ 320 degrees Celsius are preferred. In order to enhance the solubility of cyclic polyester oligomers, polymerization may be conducted through mixing them with thermoplastic polymers in a molten state. Examples of thermoplastic polymers include addition polymers such as polyethylene, polypropylene,

polyvinyl chloride, polystyrene, polyvinylidene chloride, fluororesin, polymethyl methacrylate, condensation polymers including polyamide, polyester, polycarbonate, polyphenylene oxide, polyaddition polymers such as polyurethane, and open ring polymers such as polyacetal. Among them, polyester is desirable. In polyester, polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate that are widely used, and polyester copolymers which mainly contain polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate are particularly preferred.

[0030]

Further, in the case in which thermoplastic polymers in a molten state are those polymers that passed through a preliminary polymerization tank or a final polymerization tank in a continuous polymerization process, such a method is desirable in that a static mixing device is provided in a reaction product pipe between said reaction tank and an open ring polymerization reaction tank, and cyclic polyester oligomers can be supplied through a branch pipe right before said device. Besides, thermoplastic polymers that passed through the final polymerization tank in the continuous polymerization process and then made into chips or existing thermoplastic polymers that are made into chips may be melted and mixed with cyclic polyester oligomers in an extruding machine. At this point, the extruding machine is not particularly limited, however, as examples of prior art machine, 1-axis type kneading machine, 2-axis type kneading machine and kneading machine with a vent and the like can be listed.

[0031]

Moreover, in the present invention, to improve thermal resistance and hue, prior art phosphorus compounds or cobalt compounds may be added to ultimately obtained polyester at any point. Further, in the present invention, if necessary, publicly known compounds, for example inorganic particles for frosting, antioxidant, heat insulator, antistatic agent, ultraviolet absorption agent and so forth can be added and contained.

[0032]

As described in the above, in the present invention, straight polyester oligomers for which when an esterification reaction of dicarboxylic acid and diol is conducted, the starting mole ratio of diol components and dicarboxylic acid components falls into a range of 1.0 ~ 1.6 are used for the production of cyclic polyester oligomers. Therefore, it becomes possible to obtain polyester with a high degree of polymerization more economically compared to prior art solid phase polymerization processes or open ring polymerization processes.

[0033]

[Embodiments]

Using examples in the below, the present invention is explained further in detail. Besides, physical properties in examples were measured in methods explained below.

(1) Degree of intrinsic viscosity of polymers $[\eta]$

Orthochlorophenol was used as a solvent and measurements were conducted at 25 degrees Celsius.

(2) Average polymerization degree of straight polyester oligomers

Calculations were conducted with liquid chromatography using ratio of peak surface areas for low polymers of each polymerization degree that is identified in advance (UV absorption standard : %).

[0034] Example 1

In a continuous polymerization device mainly containing a first esterification reaction tank, a second esterification reaction tank and a polycondensation reaction tank, slurry in which 16.6 part by weight of terephthalic acid and 8.2 part by weight of ethylene glycol were stirred and prepared beforehand was supplied into the first esterification reaction tank at the supplying speed of 23.8 part by weight/ hour. An average residence time at the first esterification reaction tank was 3 hours and 50 minutes, the reaction temperature was 250 degrees Celsius, the reaction pressure was 1.013×10^5 Pa, and an average polymerization degree of obtained reaction products was 3.0. This process for producing straight polyester oligomers is called Process 1.

[0035]

These reaction products were continuously extracted, and sent to a reaction tank for synthesizing cyclic polyester oligomers. In this reaction tank, α -methylnaphthalene was used as a reaction solvent, and tetraisopropyl titanate was used as a catalyst. An average residence time in said reaction tank was 50 minutes. Obtained reaction products were sent to a solvent removing tank and α -methylnaphthalene was removed. Subsequently, the reaction products were sent to a solid body precipitation tank, hexane was added, and thereby reaction products contained in the solvent precipitated. Obtained mixture was put through a centrifugal separator and a fluidized bed type dryer to be removed from hexane, and then cyclic polyester oligomers were obtained. This process to produce cyclic polyester oligomers is called Process 2.

[0036]

In addition, these reaction products were continuously extracted, and separately produced polyethylene terephthalate chips were supplied to a 2-axis type extruding machine so that the mixing ratio became oligomer/ polymer = 80/ 20. Further, as a catalyst for an open ring polymerization, tetraisopropyl titanate was added to the 2-axis type extruding machine. An average residence time at the 2-axis type extruding machine was 10 minutes, and the degree of intrinsic viscosity of obtained polyethylene terephthalate was 1.31. This process to produce polyester through open ring polymerization is called Process 3.

[0037]

Example 2

In a continuous polymerization device mainly containing a first esterification reaction tank, a second esterification reaction tank and a polycondensation reaction tank, a mixture in which 16.6 part by weight of terephthalic acid, 8.2 part by weight of ethylene glycol, and 0.002 part by weight of ethylene glycol solution containing titanium EDTA (ethylenediamine tetraacetic acid) complex against the amount of polymers to be obtained in the end (a starting mole ratio of diol components/ dicarboxylic acid components = 1.25) were stirred and prepared into a slurry beforehand. Using the slurry, polymers were polymerized in the same manner as in Example 1 except that a solvent in Process 2, an oligomer/ polymer mixing ratio and types of polymers and catalysts in Process 3 were changed. The degree of intrinsic viscosity of obtained polymers was 1.21. Polymer production was conducted within a time period that is economically superior.

[0038]

Example 3

Polymers were polymerized in the same manner with Example 1 except that propylene glycol and terephthalic acid were used as starting source materials, and a reaction solvent, catalysts and so forth were changed. The degree of intrinsic viscosity of obtained polymers was 1.18. Polymer production was conducted within a time period that is economically superior.

[0039] Example 4

Polymers were polymerized in the same manner with Example 1 except that propylene glycol and terephthalic acid were used as starting source materials, and a reaction solvent, catalysts and so forth were changed. The degree of intrinsic viscosity of obtained polymers was 1.05. Polymer production was conducted within a time period that is economically superior.

[0040] Comparative Example 1

An esterification reaction was conducted with a starting mole ratio other than that of the present invention. As a result, the polymerization degree of polymers obtained in the end was low.

[0041] Comparative Example 2

Straight polyester oligomers were produced with a starting mole ratio other than that of the present invention and butylene glycol and dimethyl terephthalate as starting source materials. As a result, the polymerization degree of polymers obtained was low. Moreover, cyclic polyester oligomers were produced using terephthaloyl chloride. However, due to influences of byproducts, the productivity in a continuous operation dropped significantly.

[0042]

[Table 1]

Process 1 (Straight oligomer synthesis)	Reaction conditions	Source material (diol/ dicarboxylic acid) Starting mole ratio Catalyst *1 (% by weight) Average residence time (hour : minute) Process type	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
			Ethylene glycol/ terephthalic acid 1:33 N/A 3:50 Continuous polymerization 3.0	Ethylene glycol/ terephthalic acid 1:25 Titanium EDTA complex 0.002 3:30 Continuous polymerization 3.9	Butylene glycol/ terephthalic acid 1:45 TBT 0.004 4:20 Continuous polymerization 2.8	Propylene glycol/ terephthalic acid 1:35 MBO 0.010 4:00 Continuous polymerization 2.5	Ethylene glycol/ terephthalic acid 1:80 N/A 4:10 Batch polymerization 1.2	Butylene glycol/ dimethyl terephthalate 2:50 TBT 0.010 4:20 Batch polymerization 1.9
Process 2 (Cyclic oligomer synthesis)	Reaction conditions	Solvent	α - methyl-naphthalene TPT 0:50	m-terphenyl TPT 1:10	α - methyl-naphthalene MBO 1:20	m-terphenyl TPT 1:10	m-terphenyl MBO 1:30	Cyclic oligomers were obtained from terephthaloyl chloride and straight oligomers.
	Average polymerization degree of reaction products	Catalyst *1 Average residence time (hour : minute)	80/ 20	70/ 30	50/ 50	30/ 70	60/ 40	However, due to influences of byproducts, the productivity in a continuous operation dropped significantly.
Process 3 (Open ring polymerization or polycondensation)	Reaction conditions	Oligomer/ polymer ratio (Polymer type) Catalyst *1 Average residence time (hour : minute)	PET TPT 0:10	PBT DBO 0:20	PET TPT 0:10	PPT TPT 0:10	PET MBO 0:30	
	Intrinsic viscosity of polymer		1.31	1.21	1.18	1.05	0.59	

*1 Catalyst: EDTA = ethylenediamine tetraacetic acid, TBT = tetrabutyl titanate, MBO = monobutylhydroxy tin oxide, TPT = tetraisopropyl titanate

[0043]

[Advantages of the Invention]

The cyclic polyester oligomer production method of the present convention enables to obtain polyester with a high degree of polymerization more economically compared to prior art production methods.

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F term (reference)	4J029	AA03	AB04	AD01	AE01	AE02
		AE03	BA02	BA03	BA04	BA05
		BA09	BA10	BD06A	BD07A	
		BF09	BF25	CA02	CA06	CA09
		CB04A	CB05A	CB06A	CC05A	
		CD03	EA05	EB04A	JA061	
		JB043	JB131	JB171	JC751	
		JF321	JF371	KB02	KB05	
		KD01	KE03	KE05	KE07	KE09
		LA02	LA05			